Photochemical Bahavior of Zinc(II) Tetraphenylporphyrin in Nanoscale-fibers Made of *trans*-1,2-Bis(alkylamide)cyclohexane Derivatives

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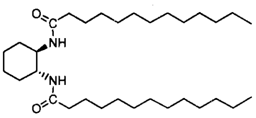
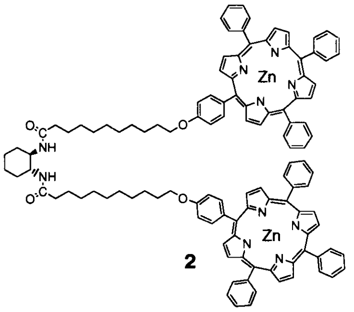
A zinc porphyrin dimer, in which two porphyrin moieties were linked with an optically active (1*R*,2*R*)- *trans*-1,2-bis(aklylamide)cyclohexane unit, was incorporated into nanoscale fibers made of organogelators and the fluorescence quenching of zinc porphyrin moieties was diminished by the incorporation.

Recently, several reports have described thermoreversible physical gelling properties of low molecular weight compounds (organogelators).[1] Most of these organogelators assemble spontaneously into ordered fibrous aggregates through noncovalent interactions. We also reported the excellent gelling ability of alkylamides derived from *trans*-1,2-diaminocyclohexane (1*R*,2*R*)-**1**, which formed nanoscopic fibrous assemblies in organic solvents through hydrogen bonding and van der Waals interactions.[2] On the macroscopic scale, this compound can form a transparent gel in organic solvents through the encapsulation of solvent into three-dimensional fibrous networks. Here we report photochemical behavior of photoactive building block **2** incorporated in the fibrous assemblies made of (1*R*,2*R*)-**1**. The photochemical behavior of metalloporphyrins and their derivatives have been investigated in micelles, polymer micelles, micellar fibers, and bilayer liquid membranes in an effort to obtain efficient photoreaction systems by mimicking the biological photosynthesis mechanism.[3] These large fibrous networks made of organogelators would provide a specific molecular environment for incorporated photoactive porphyrin molecules.[4]



(1*R*,2*R*)-**1**



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The photoactive building block **2** is readily synthesized from 5-(hydroxyphenyl)-10,15,20-triphenylporphyrin[5] as a starting material. The synthesized compound **2** has been fully characterized by UV–vis, FT-IR, MALDI-TOF mass spectrometry, and ^{1}H NMR.[6] Two zinc(II) porphyrin moieties in **2** were linked with an optically active (1*R*,2*R*)-*trans*-1,2-bis(aklylamide)cyclohexane unit. Compound **1** can gelate a wide variety of organic solvents including hydrocarbons, alcohols, ketones, and aromatic solvents. For example, the minimum amount of gel formation using **1** in toluene is only 12 mg/mL. In contrast, **2** was found to be insoluble at room temperature in most of organic solvents except for $CHCl_3$, and gel formation did not occur after dissolving in hot solvents. When a mixture of (1*R*,2*R*)-**1** and **2** ([**1**] = 12 mg/mL = 42.0 mM, [**2**] = 5.1 μM) in toluene was heated until the solid dissolved and the solution was cooled to 25 °C, a red-brown optically transparent gel was formed. This gel stayed clear for a month, and precipitation was not observed. The FT-IR spectrum of the toluene gel formed by (1*R*,2*R*)-**1** and **2** is characterized by broad bands at 3380 and 1638 cm^{-1}, which are assigned to N–H and C=O intermolecular hydrogen bonding stretching vibration, respectively. Transmission electron microscopy of a toluene gel containing **2** showed well-resolved fibrous assemblies with widths of 20–70 nm without any staining (Figure 1). On contrast, a gel made of (1*R*, 2*R*)-**1** and zinc(II) tetraphenylporphyrin (ZnTPP) lacking the *trans*-1,2-bis(aklylamide)cyclohexane unit did not produce the TEM image. The incorporation of zinc porphyrin moieties into the fibrous assemblies produced good contrast in TEM. The compound (1*R*,2*R*)-**1** was associated with formation of large fibrous assemblies through intermolecular hydrogen bonding, and **2** was incorporated into the hydrogen networks made of (1*R*,2*R*)-**1**.

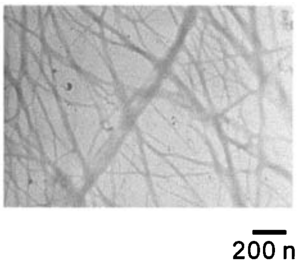

Figure 1. TEM image of a loose toluene gel prepared from (1*R*, 2*R*)-**1** and **2**.

Figure 2 shows the UV–vis and fluorescence spectra of toluene gel containing (1*R*,2*R*)-**1** and **2** at 25 °C. These spectra were nearly consistent with those of **2** in a $CHCl_3$ solution. The spectra of **2** in toluene gel did not change within the concentration range of 0.1 to 100.0 μM ([**1**] = 42.0 mM). When the gel was transformed to an isotropic solution at 50 °C, the UV–vis and fluorescence spectra were unchanged. The fluorescence lifetime of **2** in toluene gel at 20 °C was 1.5 ns, which is close

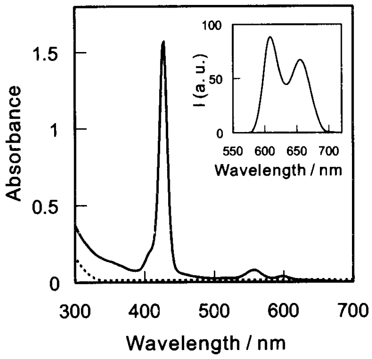

Figure 2. UV-Vis spectra of toluene gel in the absence (·····) and presence of **2** (——) at 25 °C ([(1*R*, 2*R*)-**1**] = 42.0 mM, [**2**] =5.1 μM). The inset is fluorescence spectrum of toluene gel containing **2**.

to that for **2** in a $CHCl_3$ solution (1.3 ns).[7] We previously reported that the gel of (1*R*,2*R*)-**1** exhibited strong CD peaks for the amide units due to the formation of chiral aggregates.[2] We expected that the formation of chiral aggregates might affect the orientation of porphyrin moieties. However, induced CD peaks corresponding to the absorption peaks for the zinc porphyrin moiety were not observed in toluene gel. These results indicate that the self-assembly of the organogelator (1*R*,2*R*)-**1** hardly affects the condition of the zinc porphyrin moieties.

The photochemical properties of **2** in self-assembled nanoscale-fibers were investigated by steady-state fluorescence quenching measurements using methyl viologen (MV^{2+}) as an electron transfer quenching reagent.[8] In a $CHCl_3$ solution, the fluorescence intensities of **2** and ZnTPP decreased by addition of MV^{2+}, and linear Stern–Volmer plots were obtained (Figure 3a). Normal Stern–Volmer plots in a $CHCl_3$ solution imply that this is due to an intermolecular collisional quenching. In contrast, the fluorescence intensity of **2** in toluene gel remained virtually intact while increasing MV^{2+} concentration up to 1.0 mM (Figure 3b). Under the same concentration of MV^{2+}, ZnTPP in toluene gel and **2** in an isotropic solution showed a fluorescence quenching by MV^{2+}. This difference in fluorescence quenching behaviors suggests the absolute depression of collision between zinc porphyrin moiety and MV^{2+} through incorporation into fibrous assemblies.

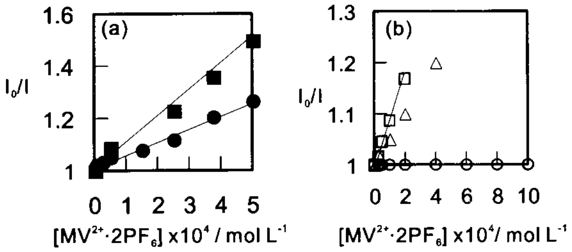

Figure 3. Stern-Volmer plots for **2** (0.53 μM) and ZnTPP (0.52 μM) in the presence of MV^{2+} $2PF_6$ in $CHCl_3$ solution (a) and toluene gel (b) ([(1*R*, 2*R*)-**1**] = 12 mg/ml) at 25(●, ○,☐, and ■) and 50 °C (△). The fluorescence intensity was monitored at 608 nm (**2** : ●,△, and ○ ; ZnTPP : ☐ and ■).

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6 **2:** mp >300 °C. FT-IR (KBr): 3286 (νNH) and 1638 cm^{-1} (νC=O). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.82 (16H, s, Pyrrole), 8.18 (16H, br, Ph), 8.08 (6H, br, Ph), 7.72 (16H, br, Ph), 5.90 (2H, br, NH), 4.25(4H, br, $-OCH_2-$), 3.62 (2H, br, cyclohexane), 1.22–2.28 (m, 44H, cyclohexane and $-CH_2-$). MALDI-TOF-MS (Dithranol): *m/z* = 1830 ($[M+H]^+$, 100), calcd for $C_{116}H_{106}N_{10}O_4Zn$: 1830.70.

7 The fluorescence decay profile of **2** in both $CHCl_3$ solution and toluene gel was well-fitted by a single exponential decay function.

8 The mixture of (1*R*, 2*R*)-**1**, **2**, and MV^{2+} in toluene was heated until the solid was dissolved. The resulting solution was cooled at 25 °C for 1h, and then the fluorescence quenching experiments were carried out.